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**APPLICATION FOR LETTERS PATENT**

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**Capacitors and Methods Of Forming Capacitors**

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**INVENTORS**

**Vishnu K. Agarwal  
Garo J. Derderian**

**EL16986 8028**

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# CAPACITORS AND METHODS OF FORMING CAPACITORS

## TECHNICAL FIELD

This invention relates to capacitors and to methods of forming capacitors.

## BACKGROUND OF THE INVENTION

Typical capacitors comprise a pair of conductive electrodes spaced apart by intervening capacitor dielectric material. As integrated circuitry becomes denser and as individual electronic components such as capacitors get smaller, integrated circuitry fabricators face the challenge of developing capacitor constructions and materials which achieve desired capacitance despite the decreasing size. Example materials under consideration for capacitor dielectric layers include titanates and tantalum pentoxide. These and other capacitor dielectric layer materials can occur in crystalline and in amorphous phases.

It is generally known that the capacitance of dielectric materials such as these can, at least initially, be increased from their as-deposited form by annealing. Such annealing can promote crystallization, re-crystallization or crystal realignment which can facilitate increase in capacitance and reduction in current leakage through the material. However, such annealing can also cause single crystals to be formed in the dielectric layer which in essence extend entirely through the

1 dielectric layer between the layer's opposing surfaces. Annealing or  
2 crystal formation to this degree can undesirably have the effect of  
3 increasing current leakage. This is primarily due to continuous paths  
4 being provided by the continuous grain boundaries for current leakage  
5 from one side of the layer to the other. It would be desirable to  
6 improve upon these adverse characteristics of capacitor dielectric layer  
7 materials.

#### 8 9 SUMMARY OF THE INVENTION

10 The invention in one aspect includes methods of forming  
11 capacitors and to capacitor constructions. In one implementation, a  
12 method of forming a capacitor includes forming a first capacitor  
13 electrode. A first layer of a first capacitor dielectric material is formed  
14 over the first capacitor electrode. A second layer of the first capacitor  
15 dielectric material is formed on the first layer. A second capacitor  
16 electrode is formed over the second layer of the first capacitor  
17 dielectric material. In accordance with another implementation, the first  
18 layer comprises a first titanate compound comprising capacitor dielectric  
19 material and the second layer comprises a different second titanate  
20 compound comprising capacitor dielectric material. A capacitor in  
21 accordance with an implementation of the invention includes a pair of  
22 capacitor electrodes having capacitor dielectric material therebetween  
23 comprising a composite of two immediately juxtaposed and contacting,  
24 yet discrete, layers of the same capacitor dielectric material. A

capacitor in accordance with another implementation includes a pair of capacitor electrodes having capacitor dielectric material therebetween comprising a composite of two immediately juxtaposed and contacting, yet discrete, layers of two different capacitor dielectric materials, said two capacitor dielectric materials including two different titanate compounds. A capacitor in accordance with still another implementation includes a pair of capacitor electrodes having capacitor dielectric material therebetween comprising a composite of two immediately juxtaposed and contacting, yet discrete, layers of two different capacitor dielectric materials, one of the two different materials comprising a titanate compound and the other comprising  $Ta_2O_5$ .

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic sectional view of a wafer fragment at one processing step in accordance with the invention.

Fig. 2 is a view of the Fig. 1 wafer fragment at a step subsequent to that shown by Fig. 1.

Fig. 3 is a view of the Fig. 1 wafer at a processing step subsequent to that shown by Fig. 2.

Fig. 4 is a view of the Fig. 1 wafer at a processing step subsequent to that shown by Fig. 3.

1 Fig. 5 is a view of the Fig. 1 wafer at a processing step  
2 subsequent to that shown by Fig. 4.

### 3 4 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 This disclosure of the invention is submitted in furtherance of the  
6 constitutional purposes of the U.S. Patent Laws "to promote the  
7 progress of science and useful arts" (Article 1, Section 8).

8 A semiconductor wafer in process in accordance with one aspect  
9 of the invention is indicated in Fig. 1 with reference numeral 10. Such  
10 comprises a semiconductive substrate in the form of a bulk  
11 monocrystalline silicon substrate 12. In the context of this document,  
12 the term "semiconductive substrate" is defined to mean any construction  
13 comprising semiconductive material, including, but not limited to, bulk  
14 semiconductive materials such as a semiconductive wafer (either alone  
15 or in assemblies comprising other materials thereon), and semiconductive  
16 material layers (either alone or in assemblies comprising other  
17 materials). The term "substrate" refers to any supporting structure,  
18 including, but not limited to, the semiconductive substrates described  
19 above. A first capacitor electrode 16 is formed over substrate 12.  
20 Exemplary materials include conductively doped polysilicon or TiN. An  
21 exemplary thickness for layer 16 is from 100 Angstroms to  
22 1500 Angstroms.

23 A first layer 18 of a first capacitor dielectric material is formed  
24 over first capacitor electrode 16. Exemplary and preferred materials

1 include barium strontium titanate (BST), strontium titanate (ST),  
2 strontium bismuth titanate (SBT), lead lanthanate zirconia titanate  
3 (PLTZ),  $\text{Ta}_2\text{O}_5$ , and mixtures thereof. The preferred method of  
4 depositing layer 18 is by chemical vapor deposition. Layer 18 as  
5 initially formed can be either crystalline or amorphous, with an initial  
6 amorphous structure being preferred and shown in the fabrication of a  
7 capacitor dielectric layer in accordance with this aspect of the invention.  
8 Regardless, first layer 18 of first capacitor dielectric material is  
9 preferably subsequently annealed at a temperature of at least  $300^\circ\text{C}$  for  
10 a time period sufficient to achieve a selected crystalline structure  
11 intended to densify and facilitate capacitive properties of such material  
12 (Fig. 2). Exemplary anneal conditions include a temperature range of  
13 from about  $300^\circ\text{C}$  to about  $1200^\circ\text{C}$  at a pressure of from about  
14 2 mTorr to about 5 atm for a treatment time of anywhere from about  
15 1 minute to 2 hours. Unfortunately as described above with respect to  
16 the prior art, such annealing can cause sufficient recrystallization to  
17 form singular grains at various locations throughout layer 18 having  
18 grain boundaries which extend from one surface of the layer to the  
19 other, as shown.

20 Referring to Fig. 3, a second layer 20 of the same first capacitor  
21 dielectric material of layer 18 is formed on first layer 18 after the  
22 preferred layer 18 annealing. Second layer 20 is also preferably  
23 chemical vapor deposited, and can initially be formed to be amorphous  
24 or crystalline. Preferably, it is initially formed to be amorphous as

1 shown. Further, the thickness of first layer 18 of the first material is  
2 preferably chosen to be from about 10% to about 90% of the finished  
3 combined thickness of first layer 18 and second layer 20. An  
4 exemplary thickness range for the combination of layers 18 and 20 is  
5 from 60 Angstroms to 1000 Angstroms. By way of example only where  
6 the material of layers 18 and 20 comprises BST, an example thickness  
7 for each layer 18 and 20 is 150 Angstroms.

8 Referring to Fig. 4, a second capacitor electrode 22 is formed  
9 over second layer 20 of the first capacitor dielectric material. An  
10 exemplary thickness range for electrode 22 is from 100 Angstroms to  
11 2500 Angstroms. Further, diffusion barrier layers, if desired, can be  
12 positioned anywhere intermediate the composite of layers 18 and 20, and  
13 first electrode 16 and second electrode 22. Regardless, it is most  
14 preferable that second layer 20 of the first material not be exposed to  
15 a temperature of 500°C or greater before deposition of any subsequent  
16 layer thereover. In certain instances, exposure to such temperature for  
17 a sufficient period of time could cause complete crystal realignment  
18 relative to the composite layer of layers 18 and 20, and undesirably  
19 form grain boundaries which extend from the base of layer 18 clear  
20 through to the top of layer 20.

21 Electrode layer 22 and/or any intervening diffusion barrier or other  
22 layer provided over layer 20 are chosen and deposited in such a way  
23 that a degree of desired stress (either tensile or compressive) will be  
24 imparted into layer 20, either during formation/deposition or subsequently

1 such as when it is heated. Such stress can be imparted inherently by  
2 the electrode material during its deposition, or by choosing  
3 deposition/forming conditions that themselves impart a desired stress.  
4 For example, selection of temperature and pressure conditions during  
5 deposition/formation of the electrode layer can be selected to impart a  
6 desired stress regardless of the electrode material being deposited.  
7 Alternately, the material can be chosen relative to the second capacitor  
8 dielectric layer to impart a desired tensile or compressive stress. Such  
9 example materials for use with the preferred titanates and pentoxides  
10 capacitor dielectric layers include  $TiN_x$ ,  $WN_x$ ,  $TaN_x$ ,  $PtRh_x$ ,  $PtRu_x$ ,  
11  $PtIr_x$ , and mixtures thereof. Further alternately, and by way of example  
12 only, the second capacitor electrode material could be doped with a  
13 conductivity enhancing impurity during its formation chosen to achieve  
14 a selected stress on the second layer of the capacitor dielectric layer.

15       Regardless, such stress can largely prevent complete  
16 recrystallization of the same material of layers 18 and 20. Exemplary  
17 dedicated anneal conditions include temperatures ranging from 500°C to  
18 1000°C, and pressures ranging from 50 mTorr to 50 atmospheres.  
19 Accordingly, layer 20 is preferably ultimately annealed either with a  
20 dedicated anneal step or in conjunction with other wafer processing to  
21 render it substantially crystalline in its finished composition. Regardless,  
22 the preferred capacitor construction will comprise a pair of capacitor  
23 electrodes having capacitor dielectric material therebetween comprising  
24



1 a composite of two immediately juxtaposed and contacting, yet discrete,  
2 layers of the same capacitor dielectric material, as shown.

3 Accordingly in the above-described preferred embodiment, first  
4 layer 18 of the capacitor dielectric layer material is essentially provided  
5 with a selected finished crystalline structure prior to formation of second  
6 layer 20 thereon. Such is achieved by the crystallization or  
7 recrystallization anneal immediately prior to formation of layer 20. Also  
8 in the preferred embodiment, the final composition of second layer 20  
9 of the first material is also desirably formed to be crystalline, although  
10 alternately such could remain amorphous if so initially deposited. In  
11 the preferred embodiment for a capacitor dielectric layer where both of  
12 layers 18 and 20 are crystalline in their final form, an interface line 19  
13 essentially forms therebetween where such discrete layers contact  
14 (Fig. 5). Interface line 19 is characterized by a perceptible change in  
15 crystallinity from one layer to the other, such as shown or evidenced  
16 in this example by a substantial lateral shift or displacement in grain  
17 boundaries from one layer to the other.

18 In accordance with another implementation of the invention, first  
19 layer 18 can comprise a first titanate compound and second layer 20  
20 can comprise a different second titanate compound. In accordance with  
21 still another implementation of the invention, first layer 18 can comprise  
22 one capacitor dielectric layer material and second layer 20 can comprise  
23 another different capacitor dielectric layer material, with one of the  
24 materials comprising a titanate compound and the other comprising

1 Ta<sub>2</sub>O<sub>5</sub>. By way of example only, example titanate compounds are those  
2 referred to above.

3 Fluorine or other grain boundary passivation treatments can also  
4 be conducted relative to the first and second layers of material  
5 intermediate or after such layers have been deposited. Example such  
6 treatments are described in our U.S. Patent No. 5,665,611 and  
- references cited therein.

8 In compliance with the statute, the invention has been described  
9 in language more or less specific as to structural and methodical  
10 features. It is to be understood, however, that the invention is not  
11 limited to the specific features shown and described, since the means  
12 herein disclosed comprise preferred forms of putting the invention into  
13 effect. The invention is, therefore, claimed in any of its forms or  
14 modifications within the proper scope of the appended claims  
15 appropriately interpreted in accordance with the doctrine of equivalents.  
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